Time and frequency dependent mechanical properties of LaCoO₃-based perovskites: Internal friction and negative creep

Mykola Lugovy,^{1,2} Nina Orlovskaya,^{1,a)} Siddhartha Pathak,³ Miladin Radovic,⁴ Edgar Lara-Curzio,⁵ Dmytro Verbylo,^{2,6} Jakob Kuebler,⁷ Thomas Graule,⁷ and Michael J. Reece⁶

¹*Department of Mechanical and Aerospace Engineering, University of Central Florida, Orlando, Florida 32816, USA*

²*Institute for Problems of Materials Science, 03142 Kiev, Ukraine*

³*Department of Chemical & Materials Engineering, University of Nevada, Reno, Nevada 89557, USA*

⁴*Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77843, USA*

⁵*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6062, USA*

⁶*School of Engineering and Materials Science, Queen Mary University of London, E1 4NS London, United Kingdom*

⁷*Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, 8600 Duebendorf, Switzerland*

(Received 20 April 2018; accepted 17 August 2018; published online 27 November 2018)

The internal friction and creep deformation behavior of La_{0.8}Ca_{0.2}CoO₃ and pure LaCoO₃ mixed ionic electronic conducting perovskite ceramics have been studied by Dynamic Mechanical Analysis and uniaxial compression under constant applied load, respectively. It was found that both the internal friction and creep strain were almost an order of magnitude higher for Ca²⁺ doped LaCoO₃ as compared to pure undoped LaCoO₃. The difference in Ca²⁺ doped LaCoO₃ behavior was attributed to the much higher concentration of point defects (e.g., oxygen vacancies) in the structure and their interaction with other mobile defects, such as ferroelastic domain/twin walls, stacking faults, dislocations, etc. Such interactions of numerous point defects with domain walls produce energetic barriers and slow down the movement of ferroelastic domain walls under applied stress. At the same time, the defects' interactions increase the internal friction resulting in a much higher creep strain of La_{0.8}Ca_{0.2}CoO₃ as compared to pure LaCoO₃, as the creep strain is determined by the distance between the domain wall and its equilibrium position at the onset of the creep process. Therefore, the high friction will result in the larger distance the wall has to move to reach the equilibrium which in turn results in higher creep strain. The expansion of LaCoO₃ under constant applied compressive stress, named here as negative creep, was also discovered to occur during room temperature creep experiments. *Published by AIP Publishing.*

<https://doi.org/10.1063/1.5037049>

I. INTRODUCTION

Time-dependent deformation behavior plays a determining role in defining the lifetime and operational conditions of brittle ceramic materials. Among many ceramics, the class of ferroelastic ceramics, often having a perovskite structure, shows distinct non-linear stress-strain behavior (Fig. 1), mostly explained by the mobility of defects, such as grain boundaries, twins, stacking faults, dislocations, and point defects during the application of external loading.^{1–3} The hysteresis, observed during loading and unloading and measured by the area enclosed by the stress-strain curves, represents the mechanical energy dissipated during deformation expressed as mechanical losses.³ The appearance and the size of the hysteresis during deformation depend on many factors, such as the types of defects and their concentration and how these defects interact with one another. The dense network of different mobile defects can easily provide stress accommodating mechanisms that can improve the

mechanical properties of ferroelastic perovskites, such as, for example, fracture toughness¹ or damping capacity; some of these stress accommodating mechanisms have been studied in depth in the past.⁴ Domain switching is one of the most characterized phenomena^{1,2} and is characterized by the switching of domains oriented in one crystallographic direction to another under load application. When domain switching occurs, the volume fraction of domains with one preferred crystallographic orientation in the twinned crystal increases upon application of the stress, while the volume fraction of domains with a second preferred crystallographic orientation decreases, when a critical stress is surpassed. If the direction of applied stress is reversed, the fraction of domains with a second crystallographic orientation starts growing while the quantity of domains with the first preferred crystallographic orientation decreases.² In domain switching or texturing of ceramics, the quantity that characterizes the size of the ferroelastic stress-strain hysteresis is the coercive stress, which is the stress necessary to reorient or destroy the domain pattern and dissipate the mechanical energy during this process. The coercive stress is determined

^{a)}Author to whom correspondence should be addressed: Nina.Orlovskaya@ucf.edu

FIG. 1. Typical stress-strain deformation curves of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites obtained under uniaxial compression. Coercive stress for both compositions is also identified in the plot.

at the inflection point of the corresponding stress-strain diagram. The mechanical energy dissipating mechanisms that produce stress-strain hysteresis include the drag of point defects, mainly oxygen vacancies, with domain walls during stress-induced domain wall movement in ferroelastic perovskite ceramics.⁵

Mechanical energy dissipation requires a relaxation process to occur in a material. This process is coupled with a strain and has a relaxation time corresponding to the frequency of the applied stress.⁶ As has already been mentioned, such relaxation processes may depend on the time dependent mobility of defects, including grain boundaries, twin walls, stacking faults, dislocations and point defects. It was reported that relaxation phenomena in LaCoO_3 , measured by Dynamic Mechanical Analysis (DMA) and Resonant Ultrasound Spectroscopy (RUS), appeared to be associated with twin wall motion, changes in spin states and low temperature magnetic polarons/dipoles. These relaxation phenomena were considered as being thermally activated processes.⁶ The overall twin wall relaxation process was reported^{7,8} to involve a spread of activation energies rather than a single, discrete thermally activated step, which is indicative of the fact that the interaction of twin walls with different defects indeed involves a variety of local mechanisms. The different pinning

characteristics of twin walls in polycrystalline LaCoO_3 were also reported to be due to variations in oxygen content in the perovskite samples.⁶ It was established that the structure of the twin walls can occupy a larger volume than the structure within the twin domains in LaCoO_3 and other perovskites.⁵ Such an increase in the size of domain walls would allow the stabilization of high spin states of Co^{3+} ions with a large ionic radius, as compared to the low spin state of Co^{3+} ions, changing the average spin state in the vicinity of the twin walls as compared to the average spin state within twin domains. It was also reported on the existence of relatively high concentrations of oxygen vacancies on the twin walls, perhaps even as clusters of vacancies or dipoles, as evidenced from the studies of twin relaxation behavior.⁶

One of the characteristic features of ferroelastic ceramics, characterized by the presence of mobile domain walls in the structure, is room temperature creep. The phenomenon of room temperature continuous deformation, called creep, was reported to occur in ferroelectric lead zirconate titanate (PZT) and BaTiO_3 ^{9–12} and ferroelastic LaCoO_3 based ceramics.^{13,14} In a similar way to the high temperature primary creep, where the materials' strain continues to increase with the strain rate slowing down with increasing strain, the room temperature creep of ferroelastic ceramics will also exhibit a decreasing creep rate with time at constant applied stress, indicating a saturation or exhaustive process.¹¹ In all of the publications, secondary creep was never found to be exhibited by ferroelastics; thus, it was concluded that room temperature creep is essentially different from that occurring in materials at high temperatures. It was reported that one of the microstructural creep mechanisms, ferroelastic domain switching, is locally consumable bringing the appearance of an equilibrium strain. Since only a finite number of domains are available to switch, it was concluded that the finite equilibrium strain would result after infinite holding time at constant applied stress.^{15,16} The schematic of such creep phenomenon is presented in Fig. 2. A new phenomenological approach for ferroelastic creep was proposed.¹³ Creep strain $\varepsilon_c = |\varepsilon - \varepsilon_0|$ can be described empirically as

$$\varepsilon_c = \Delta\varepsilon_{eq} \frac{\tilde{t}^{0.5}}{1 + \tilde{t}^{0.5}}, \quad (1)$$

where ε is the total strain, ε_0 is the strain at the beginning of constant stress stage, $\Delta\varepsilon_{eq} = |\varepsilon_{eq} - \varepsilon_0|$ is the equilibrium strain increment, ε_{eq} is the equilibrium (or saturation) strain, $\tilde{t} = t/\tau$ is the normalized time, t is the time starting from the beginning of the constant stress stage, and τ is the characteristic time. When $t = \tau$, $\varepsilon_c = \Delta\varepsilon_{eq}/2$ or half of the equilibrium

FIG. 2. Schematic presentation of a stress-strain deformation plot displaying the phenomenon of creep and negative creep in materials.

strain increment. The characteristic time of domain switching τ is a very important characteristic of the kinetics of the domain wall movement, as it can be used to characterize time-dependent processes and determine how fast or slow the domain wall movement occurs during deformation.

In all of the reported cases of creep deformation of ceramics, the strain imposed by the applied stress follows the direction of the applied stress. It means that, for example, if the applied stress is uniaxially compressive, it causes the deformation to be negative, leading to a decrease in the sample's dimension in the loading direction. Such shrinkage of the length of the sample would occur both during an increase in the applied force during loading and during the creep stage when the compressive force is held constant. Such situations were reported for PZT, BaTiO₃, LaCoO₃, and La_{0.8}Ca_{0.2}CoO₃ perovskite ceramics.^{9–13} The behavior of perovskite ceramics, described as negative creep in this paper, where upon the application of a compressive constant force, the sample deformation would occur in the direction opposite to the applied load (Fig. 2) such that, for example, a sample's length expands while the sample is held upon constant compressive force, which, to the best of our knowledge, has never been considered by anyone in the past. The similar behavior of nickel-based alloys, metallic glasses, nanocrystalline electro-deposited Ni, and zinc-aluminum cast alloy at elevated temperatures when the sample deformation occurred opposite to the applied load direction was also named “negative creep.”^{17–21} Negative creep in Refs. 17–21 was explained by a time and temperature dependent transformation of material's crystal structure including a change in the density.

The creep deformation of LaCoO₃ and La_{0.8}Ca_{0.2}CoO₃ perovskites reported in Ref. 13 was measured during relatively short periods of time of 120 s–180 s, and to our knowledge, creep experiments of longer time duration have not been reported to date, except for the measurement of room temperature creep of LaCoO₃ perovskite for a time duration of 30 min.¹⁴ In this Part I of a 2-part paper, we report our comparative findings on the temperature behavior of storage and loss moduli as well as room temperature creep behavior of La_{0.8}Ca_{0.2}CoO₃ and LaCoO₃ perovskites measured during relatively long periods of time under compression. In Part II of the paper, we report a neutron diffraction analysis of the LaCoO₃ crystal structure that was performed during *in situ* compression loading as well as a discussion of the possible explanation of such unusual behavior.

II. EXPERIMENTAL

Polycrystalline La_{0.8}Ca_{0.2}CoO₃ and pure LaCoO₃ ceramic samples were produced by Praxair Surface Technologies, Specialty Ceramics. Both La_{0.8}Ca_{0.2}CoO₃ and LaCoO₃ ceramics are single phase materials with 2–5 μ m grain size and 5%–10% of porosity. The neutron diffraction patterns of the as-sintered ceramics were measured on a Vulcan diffractometer, Spallation Neutron Source, Oak Ridge National Laboratory.^{22,23} The Rietveld refinement confirmed that both La_{0.8}Ca_{0.2}CoO₃ and LaCoO₃ had a rhombohedral structure with $R\bar{3}c$ space group (Fig. 3). The detailed characterization of structural properties of these ceramics is given.²

FIG. 3. Neutron diffraction patterns and the Rietveld refinement of LaCoO₃ (top) and La_{0.8}Ca_{0.2}CoO₃ (bottom). The refinement confirms the rhombohedral structure ($R\bar{3}c$ space group) and the high purity of both as-sintered LaCoO₃ and La_{0.8}Ca_{0.2}CoO₃. Lattice parameters of LaCoO₃: $a = 5.44301(8)$ Å, $c = 13.0963(3)$ Å; lattice parameters of La_{0.8}Ca_{0.2}CoO₃: $a = 5.43239(8)$ Å, $c = 13.0969(3)$ Å.

Test specimens for compression creep testing consisted of a cylinder of 6 mm in diameter and 12 mm in length, while $20 \times 8 \times 1$ mm³ bars, machined by PremaTech Ceramics, were used for Dynamic Mechanical Analysis (DMA).

DMA tests were carried out on La_{0.8}Ca_{0.2}CoO₃ and LaCoO₃ samples using a single cantilever clamp set-up in a Q800 instrument (TA instruments, IL, USA). A sinusoidal stress producing 2 μ m constant displacement amplitude (or 0.0036% of constant strain amplitude) was applied to the sample, while the corresponding strain signal and the phase lag δ between the stress and strain were recorded.²⁴ The length of the sample clamp was 17.5 mm. The data were recorded during heating up to 600 °C with a heating rate of 3 K/min and for stress frequencies of 0.1, 1, 10, and 100 Hz. The 2 μ m amplitude of the samples' displacement was chosen as sufficiently high to obtain large mechanical loss peaks in DMA experiments; yet, its amplitude was low enough to avoid cracking or failure of the cobaltite samples.

Uniaxial compression was conducted to produce stress-strain and creep strain deformation plots of cobaltites both

during continuous loading and during long time duration creep experiments, respectively. A servohydraulic universal testing machine (Instron mod. 8511, UK) with a 20 kN load cell was used to subject the cylindrical test specimens to compressive loading along the length of the cylinders. At the beginning of the experiments, the sample was preloaded to 5 MPa and then the load was set to zero, followed by compression testing in load control mode using a loading/unloading rate of 3 MPa/s. For the continuous loading tests, the sample was continuously compressed until the stress reached the desired stress level followed by complete unloading without application of any dwell time at any applied stress level. For the creep strain, the sample was loaded either to the coercive stress σ_{coer} , which was measured to be equal to 134 MPa for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and 70 MPa for LaCoO_3 ,¹³ or to stresses slightly below or above the coercive stress, and then the sample was held at this constant stress for a predetermined period of time. The axial strain was measured using three strain gauges (FLA-3-11-1L, Tokyo Sokki Kenkyujo Co., Ltd, Japan) mounted on the surface of each sample. After careful alignment of the sample, the total strain was determined by averaging the signals from the three strain gauges. All experiments were performed at room temperature and 40% relative humidity.

III. RESULTS AND DISCUSSION

A. Storage modulus, loss modulus, and internal friction

Similar to many other ferroelastic ceramics with a second order continuous phase transition,^{25,26} internal friction peaks were found to exist when the elastic and anelastic properties of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites were studied using DMA (Fig. 4). Such information on internal friction peaks, which are indicative of mechanical loss or damping during anelastic dissipation of mechanical energy, could be combined with the characteristic relaxation times for the domain wall movement, thus giving the chance to distinguish different anelastic loss mechanisms to better understand the ferroelastic time dependent deformation behavior of cobaltites. The elastic modulus and the mechanical damping behavior of cobaltites as a function of temperature and frequency are shown in Figs. 4 and 5. Both the real part E' (storage modulus) and the imaginary part E'' (loss modulus) of the elastic modulus $E = E' + iE''$ in a wide frequency (0.1 Hz–100 Hz) and temperature (RT to 600 °C) range are shown for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites in Figs. 4(a) and 4(b), respectively. The mechanical damping $\tan \delta = E''/E'$ or internal friction of the two cobaltites as a function of temperature for different frequencies is shown in Fig. 5.

The storage modulus of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ decreases from 88 GPa at room temperature to 40 GPa at 600 °C, but such change in E' is much less for pure LaCoO_3 whose storage modulus decreases smoothly from 55 GPa at room temperature to 45 GPa at 600 °C (Fig. 4). As one can see from Fig. 4, the storage modulus of both $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and pure LaCoO_3 perovskites decrease first linearly at the beginning of heating; however, for both compositions, there is a decrease

FIG. 4. Temperature and frequency dependencies of real (storage modulus) and imaginary (loss modulus) parts of the elastic modulus of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites.

in the storage modulus in-between 100 °C ($E' = 80$ GPa) and 400 °C ($E' = 45$ GPa) for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and in-between 200 °C ($E' = 49$ GPa) and 350 °C ($E' = 45$ GPa) for LaCoO_3 . This decrease is much less pronounced for pure LaCoO_3 , which, in fact, looked more like a change in the slope at ~ 300 °C and occurred in a more narrow temperature range and to a much smaller degree than for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ perovskite. The loss modulus E'' of two perovskites versus

FIG. 5. Comparison of temperature and frequency dependencies of internal friction in $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites.

temperature is also shown in Fig. 4. Strong loss modulus peaks can be seen for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ in the 100–300 °C temperature range where both storage and loss moduli show frequency dependence in the measured temperature range. Such correlations in storage and loss moduli high temperature behavior suggests that the significant decrease in the storage modulus of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ perovskite from 80 GPa at 100 °C to 45 GPa at 400 °C is caused by mechanical damping, as during the damping events the vibrations between atoms/ions in the lattice are increased causing the increase in the bond length and, as a result, in bond weakening, resulting in significant softening of the material. The very same behavior in terms of simultaneous softening and increase in the damping capacity has been reported for typical viscoelastic materials.²⁷ At higher frequencies, the loss peaks shift to higher temperatures in $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and their intensities also increase [Fig. 4(a)]. The loss modulus E'' of LaCoO_3 is also shown in Fig. 4 as a function of temperature; however, its values are much smaller (~ 1.2 GPa) in comparison with the much higher values (~ 8 GPa) of E'' for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$. Also, in the case of pure LaCoO_3 , while there is a certain degree of correlations between the frequency dependence of E' and E'' behavior was also detected, it was found that the correlation is much weaker than was observed for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ perovskite. While more pronounced E'' loss peaks were measured at the lower frequencies of 0.1 Hz and 1 Hz, at higher frequency 10 and 100 Hz tests, they became almost invisible, while some disruption and discontinuity jumps in the data appeared in the 300 °C temperature range for the DMA results of LaCoO_3 [Fig. 4(b)].

The comparison of mechanical damping, represented as $\tan \delta = E''/E'$ for both $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites, is shown in Fig. 5. As one can see from Fig. 4, the internal friction in $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ is 5–7 times higher than in LaCoO_3 . Such a large difference in the internal friction and materials' damping capacity could be explained both by the availability and the mobility of defects existing in the perovskite structure. It is known that both the $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 compositions crystallize with a rhombohedral $R\bar{3}c$ structure and both are heavily twinned materials. The rhombohedral distortion is the highest for LaCoO_3 with a value of α rhombohedral angle equal to 60.815° at room temperature, while the rhombohedral distortion decreases to $\alpha = 60.695^\circ$ at room temperature for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ because of doping. Such changes in crystallography might affect the mobility of the twin boundaries, as well as the materials' damping capacity during applied stress both as a function of frequency and temperature. In addition, doping LaCoO_3 with divalent Ca^{2+} ions introduces significant oxygen nonstoichiometry, and thus numerous oxygen vacancies in the lattice.²⁸ The presence of these point defects definitely affects the damping capacity of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ perovskite as compared to more stoichiometric LaCoO_3 , as the internal friction in $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ is significantly increased due to the fact that numerous point defects interact and interfere with moving domain walls, making their velocity much slower and movement more difficult while they drag numerous oxygen vacancies and their complexes along the pathway.

The damping peaks during anelastic relaxation represent energy dissipated during mechanical loading at different frequencies due to movement of defects and such frequency dependence, especially in the case of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ perovskite, indicates that the underlying mechanism is a thermally activated process. Since the peak positions depend on the frequency, one can apply the Arrhenius equation to the relaxation rate

$$\tau^{-1} = \tau_{\infty}^{-1} \exp\left(-\frac{H_r}{kT}\right), \quad (2)$$

where τ^{-1} is the relaxation time, frequency $f = 1/\tau$, H_r is the activation energy of the relaxation process, τ_{∞}^{-1} is related to atomic jump rates inherent to the specific relaxation mechanism, k is the Boltzmann constant, and T is the temperature in Kelvin. The activation energy H_r required for the process can be estimated from the slope of the straight line of $\ln f$ versus $1/T$. Once the activation energy is known, the exact underlying mechanism causing the appearance of loss modulus peaks can be inferred.

In order to perform the H_r calculation, the positions of the loss modulus peaks were determined by curve fitting. The best fit for both $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites' loss modulus peaks was obtained by fitting three peaks with the data shown in Fig. 4. Fitting peaks are not shown in the paper for brevity. The frequency and the temperature of each of these three deconvoluted peaks obtained assuming a single Debye relaxation model²⁴ were plotted in an Arrhenius type ($\ln f$ vs $1/T$) plot in Fig. 6. The activation energies for these peaks were calculated from the slope of the best fitted lines in Fig. 6 according to Eq. (2) and their values are summarized Table I.

It was found that for all three peaks assigned to the $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ perovskite, the mechanical loss peaks shifted to higher temperatures and higher intensities with increasing frequency, which indicates that the process responsible for damping of all three peaks is thermally activated,^{24,29} where the maximum internal friction is defined as $\tan \delta_{\max} = \Delta/2$, where $\tan \delta_{\max}$ is mechanical damping when $\omega\tau = 1$, Δ is the relaxation strength and $\omega = 2\pi f$ is the angular velocity, f is the frequency of strain oscillation, and δ is the phase lag between stress and strain as defined.²⁴ As published,⁶ the appearance of the peak with an activation energy of 2.24 eV can be explained by the movement of the domain walls, while the appearance of peaks with either lower than 1.32 eV or higher than 1.83 eV activation energies can be explained by the existence and movement of numerous oxygen vacancies, which form different dipoles with cobaltite ions in the lattice of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$. As one might assume, the movements and interactions of both twin walls and numerous oxygen vacancy point defects are responsible for the high internal friction inside the lattice, which possibly slows down the mobility of these defect complexes.

For pure LaCoO_3 , the much higher activation energy equal to 3.27 eV was found for one of the three peaks, which shows a frequency dependence, and thus it is clear that the underlying mechanism responsible for the process is thermally activated. This high activation energy $H_r = 3.27$ eV

FIG. 6. Arrhenius plots for three fitted peaks of loss modulus vs temperature plots for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites.

value is higher than $H_r = 1.91$ eV, which was assigned to the movement of the domain walls in LaCoO_3 and reported.⁶ The two other peaks, both located in the 285 °C–340 °C temperature range, showed infinite values, and thus are frequency independent. While such frequency independence of the mechanical loss was reported as typical for the first order phase transformations,^{4,24} no phase transition was ever discovered in this temperature range of 250 °C–400 °C in pure LaCoO_3 .³⁰ However, the spin state in Co^{3+} ions and the semiconductor to metal transitions were studied and reported to occur around 230 °C, bringing numerous changes in both the thermal and electrical properties of pure LaCoO_3 .^{31,32} In addition to the two frequency-independent loss modulus peaks, jumps were also recorded during data collection, suggesting the existence of some very fast, almost instantaneous processes. The DMA results obtained on two cobaltite

TABLE I. Activation energy of loss modulus peaks.

	$\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$	LaCoO_3
1st loss modulus peak	1.32 eV	3.27 eV
2nd loss modulus peak	1.83 eV	...
3rd loss modulus peak	2.24 eV	...

compositions provide clear evidence that the values for the loss factor of LaCoO_3 (~ 0.025), while still much higher than many other engineering ceramics ($\sim 10^{-3}$),³³ are still much lower in comparison with $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ (~ 0.14). Such difference in the internal friction of two materials (Fig. 5) can be explained by the fact that, as a first approximation, while we can assume that the amount of the mobile defects, such as twin walls and stacking faults is very similar in both compositions, the number of point defects is much higher in Ca doped LaCoO_3 . Therefore, the mechanical losses and the internal friction occurring in this material are much more dramatic as compared to pure LaCoO_3 because of the numerous oxygen vacancies, and their complexes restrict and pin the domain wall movement by interacting more strongly and residing inside of the domain walls in much higher quantities in $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$.

B. Creep strain

The creep strain as a function of time measured for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and pure LaCoO_3 perovskites is shown in Fig. 7. As it was previously established in Ref. 13, the creep strain is larger when the perovskite ceramic is loaded to the coercive stress level, located at the inflection point of the loading part of the stress-strain deformation plot (Fig. 1). The coercive stress of 134 MPa was measured for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$

FIG. 7. Creep strain as a function of time measured at a constant stress of 134 MPa for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and at a constant stress of 70 MPa for LaCoO_3 perovskites.

and 70 MPa for LaCoO_3 perovskites, and these stress levels were used as the constant stress for the creep testing of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 samples presented in Fig. 7, respectively. As it was discussed in detail,¹³ the creep strain of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ exhibits a decrease in the creep rate with time at a constant applied stress [Fig. 7(a)], indicating a saturation or exhaustive process. The direction of the creep strain measured on $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ follows the direction of the applied compressive stress leading to a further shrinkage of the length of the sample, as the load applied during the experiment is a compressive one. It was expected to observe a similar creep strain behavior for pure LaCoO_3 perovskite composition; however, the measured data show completely different and very unusual behavior [Fig. 7(b)]. To the best of our knowledge, such behavior has never been reported before for ferroelastic ceramics in the past. As one can see from Fig. 7(b), the creep strain of LaCoO_3 measured during the first 1800 s of the experiment showed initially an increase in creep strain with a decrease in the creep rate with time at a constant applied stress, similar, but about one order of magnitude smaller, to the behavior exhibited by $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ [Fig. 7(a)]. However, at test times longer than 1800 s, the creep strain started decreasing, which indicated an axial expansion of the sample, while still under constant compressive stress of 70 MPa.

To verify, if such an expansion of the sample upon applied constant compressive stress was not an experimental artifact, additional tests were carried out at three different constant stress levels: (a) 44 MPa, which lies below 70 MPa coercive stress; (b) 70 MPa, which is at the coercive stress; and (c) 110 MPa, which lies above 70 MPa coercive stress of LaCoO_3 . The results of this experiment are shown in Fig. 8, where, as one can see, the expansion (negative creep) of the sample kept under a constant applied compressive load occurs in all three cases, but it becomes more pronounced with an increase in the applied constant stress (i.e., the negative creep is the least pronounced when the sample was loaded at 44 MPa which is below LaCoO_3 's coercive stress, and it became very visible for the test performed at 70 MPa,

FIG. 8. Creep strain measured for LaCoO_3 samples at constant compressive stress of 44 MPa (below coercive stress), 70 MPa (at coercive stress), and 110 MPa (above coercive stress). Experiments were conducted at Queen Mary University of London.

FIG. 9. Creep strain in LaCoO_3 measured at a constant stress of 70 MPa for 5.68 days.

and even higher negative creep became visible when the sample was preloaded to 110 MPa above LaCoO_3 's coercive stress value. By simply looking at the plots presented in Figs. 7(b) and 8, two parts of the creep strain curves could be clearly distinguished. The first part of the curve appeared during the initial portion of the creep strain versus time plots, where the time is equal to or does not exceed about 1800 s. In this part, the creep strain values increase as a function of time with the strain rate decreasing up to the point when creep strain reaches a maximum value. After reaching the maximum, the creep strain begins to decrease with increasing strain rate and then with a decreasing strain rate as a function of time.

To verify the above behavior, even longer creep experiments on LaCoO_3 were performed, where the dwell time at 70 MPa constant compressive stress was extended from 15 000 s (4.17 h) to 491 000 s (5.68 days). The results of such long experiments (5.68 days) on the creep strain are shown in Fig. 9. As one can see from Fig. 9, both creep (shrinkage) followed by negative creep (expansion) of LaCoO_3 were recorded within first 4 h of the test. Then, periodic cyclic variations in creep strain as a function of time were recorded for the rest of 132.32 h. Upon an analysis of these periodic fluctuations, it was established that they occurred within 24 h and coincide with the occurrence of day and night periods in the lab. As the temperature in the laboratory, where the experiments were performed, was not controlled by a thermostat, it was assumed that the temperature apparently equilibrates for a couple of degree difference during the day and night periods due to the difference in the outside temperature, and this difference in the surrounding environment was the reason for the expansion and contraction of the sample, as measured by the strain gauges. The explanations for the possible origin of the negative creep in LaCoO_3 are discussed in Ref. 34.

IV. CONCLUSIONS

The ferroelastic behavior of LaCoO_3 based perovskites results in hysteresis and mechanical energy dissipation during material's deformation upon loading. This energy dissipation requires the relaxation processes and time dependent behavior, such as creep, to occur in these materials. Both relaxation processes and creep deformation depend on the availability and mobility of the defects, such as grain boundaries, twin walls, stacking faults, dislocations, and point defects or even occurrence of the phase transition in the perovskites during loading. It was established that in cobaltites, much higher internal friction $\tan \delta$, directly associated with

the loss modulus measured by DMA, occurred in $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ perovskite ceramic as compared to pure LaCoO_3 . Much higher $\tan \delta$ values were found to be associated with the presence of much higher quantities of oxygen vacancies in the crystal lattice of Ca^{2+} doped LaCoO_3 formed due to the need to maintain the charge neutrality. These vacancies interact with the domain walls, acting as pinning points to the domain walls and slowing them down and preventing them from moving fast. At the same time, the availability and the mobility of these defects affected not only hysteresis measured in stress-strain deformation or frequency dependent internal friction, but it also defined time dependent room temperature creep deformation of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites measured during uniaxial compression. It was found that room temperature creep strain of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ showed a decrease in the creep rate with time at the constant applied coercive stress $\sigma_{\text{coer}} = 134$ MPa, indicative of a saturation process. The creep strain of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ perovskite led to further shrinkage of the sample length, which was in perfect agreement with the direction of the applied compressive stress. However, the creep strain of LaCoO_3 showed very different behavior, such that, at first, it showed an increase in the creep strain indicative of the sample's contraction, followed by a decrease in the creep strain, which indicated an axial expansion of the sample all that occurred at a constant applied compressive stress. The appearance of such expansion of the sample under applied compressive stress was termed "negative creep" in this article. It was also shown that the negative creep was a function of constant applied compressive stress, as the expansion of the sample increased when constant stress increased from 44 MPa (below coercive stress) to 70 MPa (at coercive stress) and to 110 MPa (above coercive stress of LaCoO_3). It is also important to notice that while in many compressive experiments we performed the negative creep of LaCoO_3 was detected, while in our many other time-dependent experiments LaCoO_3 exhibited an ordinary creep deformation when only shrinkage of the sample was measured during the application of constant applied compressive stress. The reasons for such different behavior are still to be found out.

ACKNOWLEDGMENTS

This work was supported in part by the NSF Project No. CMMI-0968911, "Time Dependent Creep Deformation of Non Polar Mixed Conducting Ferroelastic Perovskites". John Lloyd's help with the DMA measurements of temperature and frequency dependent real and imaginary parts of elastic modulus of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and LaCoO_3 perovskites during his stay at Oak Ridge National Laboratory in 2004 is acknowledged. The neutron diffraction experiment was carried out at the Spallation Neutron Source at Oak Ridge National Laboratory, which is one of the user facilities sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. The authors thank Mr. H. D. Skorpenske from SNS for the technical support of the neutron experiment. M.R. is thankful to the NSF Ceramics Program for supporting this study through Grant No. 1057155

awarded to Texas A&M University. S.P. acknowledges the support from the 2005 SURF-ORNL (the Southeastern Universities Research Association) Summer Cooperative Research Program scholarship and the thesis grant from Empa, Dübendorf, Switzerland for this work. Work at the Oak Ridge National Laboratory was sponsored by the U.S. Department of Energy, Office of Fossil Energy, Solid Oxide Fuel Cells Program, Core Technology Program at ORNL.

- ¹N. Orlovskaya, Y. Gogotsi, M. J. Reece, B. Cheng, and I. Gibson, *Acta Mater.* **50**, 715 (2002).
- ²N. Orlovskaya, N. Browning, and A. Nicholls, *Acta Mater.* **51**, 5063 (2003).
- ³N. Orlovskaya, H. Anderson, M. Brodnikovskyy, M. Lugovy, and M. J. Reece, *J. Appl. Phys.* **100**, 026102 (2006).
- ⁴*Mechanical Spectroscopy Q-1 2001*, edited by R. Schaller, G. Fantozzi, and G. Gremaud (Trans Tech Publications Inc., Uetikon-Zuerich (CH), 2001).
- ⁵L. Goncalves-Ferreira, S. A. T. Redfern, E. Artacho, E. Salje, and W. T. Lee, *Phys. Rev. B* **81**, 024109 (2010).
- ⁶Z. Zang, J. Koppensteiner, W. Schranz, D. Prabhakaran, and M. A. Carpenter, *J. Phys. Condens. Matter* **23**, 145401 (2011).
- ⁷R. J. Harrison, S. A. T. Redfern, and J. Street, *Am. Miner.* **88**, 574 (2003).
- ⁸R. J. Harrison, S. A. T. Redfern, and E. K. H. Salje, *Phys. Rev. B* **69**, 144101 (2004).
- ⁹D. Zhou and M. Kamlah, *Acta Mater.* **54**, 1389 (2006).
- ¹⁰T. Fett and G. Thun, *J. Mater. Sci. Lett.* **17**, 1929 (1998).
- ¹¹J. S. Forrester and E. H. Kisi, *J. Eur. Ceram. Soc.* **24**, 595 (2004).
- ¹²E. C. Subbarao, M. C. McQuarrie, and W. R. Buessem, *J. Appl. Phys.* **28**, 1194 (1957).
- ¹³M. Lugovy, V. Slyunyayev, N. Orlovskaya, D. Verbylo, and M. J. Reece, *Phys. Rev. B* **78**, 024107 (2008).
- ¹⁴W. Araki, T. Abe, and Y. Arai, *J. Appl. Phys.* **116**, 043513 (2014).
- ¹⁵G. Viola, K. B. Chong, F. Guiu, and M. J. Reece, *J. Appl. Phys.* **115**, 034106 (2014).
- ¹⁶K. B. Chong, F. Guiu, and M. J. Reece, *J. Appl. Phys.* **103**, 014101 (2008).
- ¹⁷P. Hahn, M. Schwienheer, C. Kontermann, and M. Oechsner, *Materialwiss. Werkstofftech.* **48**, 1070 (2017).
- ¹⁸J. S. Kirkaldy, *Mater. Sci. Eng. A* **409**, 167 (2005).
- ¹⁹P. T. Vianco and J. C. M. Li, *Mater. Sci. Eng.* **95**, 175 (1987).
- ²⁰S. Van Petegem, S. Brandstetter, H. Van Swyghoven, and J.-L. Martin, *Appl. Phys. Lett.* **89**, 073102 (2006).
- ²¹X.-w. Wei, and B.-I. Shen, *Trans. Nonferrous Met. Soc. China* **13**, 818 (2003), available at http://www.tnmsc.cn/paper/paperView.aspx?id=paper_13992.
- ²²X. L. Wang, T. M. Holden, A. D. Stoica, K. An, H. D. Skorpenske, A. B. Jones, G. Q. Rennich, and E. B. Iverson, *Mater. Sci. Forum* **652**, 105 (2010).
- ²³K. An, H. D. Skorpenske, A. D. Stoica, D. Ma, X. L. Wang, and E. Cakmak, *Metall. Mater. Trans. A* **42**(1), 95 (2011).
- ²⁴P. Gao, E. Lara-Curzio, R. Trejo, and M. Radovic, *J. Electrochem. Soc.* **162**(1), F14 (2015).
- ²⁵F. Yan, X. Chen, P. Bao, and Y. Wang, *J. Appl. Phys.* **87**, 1453 (2000).
- ²⁶H. Frayssignes, M. Gabbaya, G. Fantozzi, N. J. Porchb, B. L. Chengc, and T. W. Buttonb, *J. Eur. Ceram. Soc.* **24**(10–11), 2989 (2004).
- ²⁷Y. N. Wang, Y. N. Huang, H. M. Shen, and Z. F. Zhang, *J. Phys. IV France* **6**, C8-505 (1996).
- ²⁸H. U. Anderson, *Solid State Ionics* **52**, 33 (1992).
- ²⁹A. Lakki, R. Herzog, M. Weller, H. Shubert, C. Reetz, O. Gorke, M. Kilo, and G. Borshardt, *J. Eur. Ceram. Soc.* **20**, 285 (2000).
- ³⁰A. Aman, R. Jordan, Y. Chen, R. Stadelmann, M. Lugovy, N. Orlovskaya, E. A. Payzant, C. dela Cruz, M. J. Reece, T. Graule, and J. Kuebler, *J. Eur. Ceram. Soc.* **37**, 1563 (2017).
- ³¹N. Orlovskaya, D. Steinmetz, S. Yarmolenko, D. Pai, J. Sankar, and J. Goodenough, *Phys. Rev. B* **72**, 014122 (2005).
- ³²M. A. Señaris-Rodriguez and J. B. Goodenough, *J. Solid State Chem.* **116**(2), 224 (1995).
- ³³M. F. Ashby, *Acta Metall.* **37**, 1273 (1989).
- ³⁴M. Lugovy, A. Aman, N. Orlovskaya, V. Slyunyayev, T. Graule, J. Kuebler, M. J. Reece, Y. Chen, D. Ma, and K. An, *J. Appl. Phys.* **124**, 205104 (2018).